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Ion implantation of porous silicon

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We have investigated the properties of light-emitting porous silicon after ion implantation and successive annealing through continuous-wave photoluminescence (CWPL) and time dependent photoluminescence (TDPL) spectroscopies. Implantation was performed with phosphorus, boron and silicon ions of different doses and energies. Low dose dopant implantation keeps or even increases the CWPL intensity and increases the TDPL decay time. High dose dopant implantation and silicon self-implantation reduce the CWPL intensity and slightly decrease the TDPL decay time.

Due to its efficient and visible photoluminescence (PL) at room temperature and its natural compatibility with crystalline silicon, light emitting porous silicon (LEPSi) is a promising material for silicon-based optoelectronics devices. Several light-emitting devices (LEDs) have been reported.^{1,2} It appears that, in terms of quantum yield of the LEDs, *p-n* junctions or *p-i-n* structures should be superior to other geometries.²

It has been observed that the resistivity of LEPSi becomes higher than $10^5 \Omega \text{ cm}$ independent of the doping level of the silicon substrate.³ This can be explained by the quantum confinement model⁴ in which the band gap of the Si nanostructures increases and the Fermi level moves towards the middle of the band gap. Many device structures would require doping after the formation of LEPSi. Ion implantation⁵ and thermal diffusion are two major techniques widely used in modern silicon microelectronic technology. Diffusion can produce a relatively homogeneous doping region with few defects but requires a very high temperature for a long period of time. This is not appropriate for LEPSi because long duration high temperature treatment reduces the PL intensity and changes the PL peak energy.⁶ Ion implantation, on the other hand, is a technique in which the dopant atoms are vaporized, accelerated, and directed to a substrate kept at room temperature. The doping depth and the concentration can be controlled easily by the acceleration energy and the beam current, respectively. As each ion impinges on the substrate, it undergoes a series of nuclear collisions causing damage to the silicon lattice. The damage can be eliminated by annealing which also results in the activation of the implanted dopants. Ion implantation has the advantages of shallow doping length and doping controllability. However, its effects on the light emitting properties of LEPSi have not yet been studied.

LEPSi layers were fabricated by anodizing *n*-type (100) silicon substrates in a 50% HF:CH₃OH=1:1 (volume) solution for 40 min under white light illumination.⁶ The anodization current density was 6 mA/cm². The porous layer thickness was approximately 80 μm as revealed by cross-sectional microscopic measurement. However, light emission

typically occurs in the first 5–10 μm of the porous layer.^{7,8}

The continuous-wave PL (CWPL) spectrum was excited by the 4579 Å Ar⁺ laser line and was recorded by a grating spectrometer attached to an optical multichannel analyzer (OMA). Time dependent PL (TDPL) experiments used a frequency tripled Q-switched Nd:YAG laser producing 7 ns pulse width at 355 nm. A photomultiplier attached to a monochromator was used to record the PL decay at different wavelengths. At room temperature, the PL decay is not exponential⁹ and is adequately described by a stretched exponential.¹⁰ With our signal to noise ratio, the decay can be fitted simply by a fast exponential component, followed by a much slower component.

Ion implantation was performed using silicon (Si), boron (B), and phosphorus (P) at an energy of 150, 75, and 170 keV, respectively. The implantation dose varied from 1×10^{12} to $1 \times 10^{15} \text{ cm}^{-2}$. The ions were implanted 7° off the normal to the substrate. Some samples were then thermal annealed in N₂ at a temperature of 850 °C for 30 min.

The resistivity after ion implantation was measured by the four point probe method. Although there were variations in the results at different points of the samples due to the difficulty in making a good contact between the probes and the LEPSi layer, the trends were obvious. The resistivity of the reference LEPSi layer is about 1.6 M $\Omega \text{ cm}$. The resistivity of the boron implanted samples was always much higher than the reference sample (e.g., 45.7 M $\Omega \text{ cm}$ for a dose of 10^{13} cm^{-2}) but it decreased when increasing the implantation dose. Phosphorous implanted samples, however, have a lower resistivity than the reference sample (e.g., 0.9 M $\Omega \text{ cm}$ for a dose of 10^{13} cm^{-2}) and the resistivity decreased with increasing implantation dose. Silicon implantation does not change the resistivity of LEPSi. Hot probe test¹¹ was performed at the same time. The orientation of the voltage obtained in the measurement indicated that the conduction carriers in boron implanted LEPSi layers were different from that of the reference samples. This implies that the majority carrier type and concentration in LEPSi can be changed by ion implantation.

Computer simulations (by SUPREM IV) of the dopant pro-

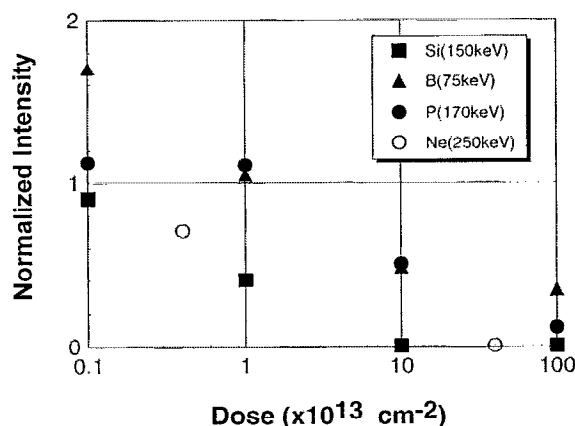


FIG. 1. Changes of the PL intensity (average of several measurements) with implantation dose for different ions. The intensities are normalized to the PL intensity of unimplanted LEPSi. Results of Ne ion implantation from Ref. 13 are given for comparison.

file after ion implantation and after annealing were carried out for LEPSi with 70% porosity by simply reducing the density to 30% of crystalline silicon. The resulting junction depth is calculated to be 0.7 for B and 1.0 μm for P, twice as deep as for crystalline silicon. The post-implant annealing does not increase the junction depth appreciably since the thermal-diffusion depth of P and B is only about 0.01 μm under our annealing condition.

The excitation laser wavelengths used in the experiments have a penetration depth of $\sim 0.5 \mu\text{m}$ in LEPSi¹² which guarantees that the CWPL and TDPL results come from the implanted region only. Changes of the CWPL intensity and peak position after ion implantation were carefully recorded with respect to a reference sample. All PL peaks were red shifted by about 40 meV after ion implantation. As shown in Fig. 1, low dose dopant implantation does not reduce the PL intensity very much and even enhances it in some cases. Si implantation and higher dose dopant implantation quench the PL. In Fig. 1, we compare our results to those of Barbour *et al.*¹³ obtained after neon (Ne) ion implantation. Their results show strong PL quenching after implantation which is not inconsistent with our results for Si ion implantation.

TDPL was recorded before and after ion implantation. The measured PL decay is wavelength dependent.⁹ At the CWPL peak wavelength, the fast component of the decay of unimplanted LEPSi was approximately 4 μs (Fig. 2). Low dose dopant implantation not only increased the PL intensity as discussed above but it also increased the decay time to 9 μs . On the other hand, high dose dopant implantation and silicon self-implantation slightly reduced the decay time.

The PL quenching and the change in PL decay time after implantation can be explained by the formation of nonradiative centers in the band gap. Since the room temperature PL decay time is dominated by nonradiative processes,⁹ the slight decrease in decay times should be related to an increase in the number of nonradiative centers. In contrast, the increase of the decay time after dopant implantation at low doses suggests that the passivation or elimination of nonra-

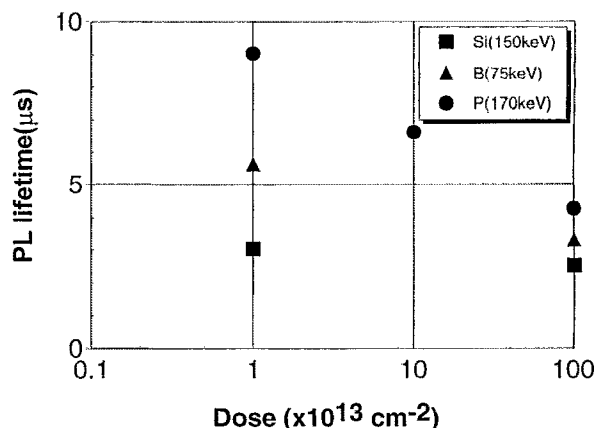


FIG. 2. Changes of the PL lifetime with implantation dose for different ions. The PL lifetime of unimplanted LEPSi sample is 4 μs .

diative centers has taken place, which is also the reason for the slight increase of the CWPL intensity.

Annealing generally causes a reduction of PL intensity in all samples implanted with dopants (phosphorus or boron). However, for high dose silicon self-implantation, annealing restored partially the PL intensity (Fig. 3). We interpret this behavior as a competition between the removal of the damage introduced by ion implantation and the elimination of the surface hydrogen which passivates the surface. Thus, for heavily damaged samples, the damage removal process is more important, causing a partial recovery of the PL intensity. For the less damaged samples, the PL intensity is reduced due to the loss of hydrogen. The difference between the relative intensity of the P-implanted and B-implanted samples after annealing may be due to the different profiles of the electric field in the n^+/n and p/n junctions, respectively. Further research will establish whether this difference is statistically meaningful.

From our work, it appears that LEPSi survives dopant ion implantation at low to medium doses. As indicated by our computer simulations, implantation with a dose of about 10^{13} cm^{-2} is enough to compensate the substrate doping level of $3 \times 10^{15} \text{ cm}^{-3}$. From our CWPL results, there is

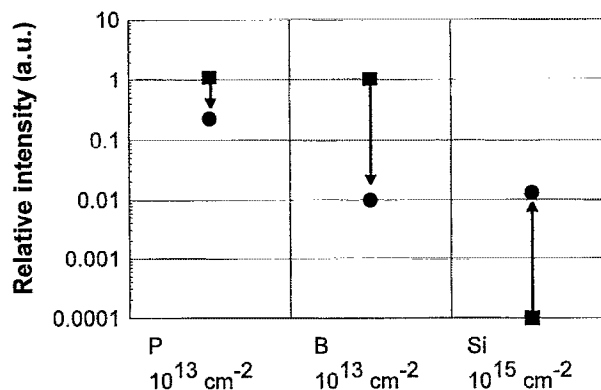


FIG. 3. PL intensity of ion implanted LEPSi samples before annealing (■) and after annealing (●). The intensities are normalized to the PL intensity of unimplanted LEPSi.

clearly no significant changes in the PL intensity for this implantation dose. This implies that a p - n junction can be formed by ion implantation of LEPSi without changing appreciably the light emitting properties.

In conclusion, the effects of ion implantation on the resistivity and the light emitting properties of porous silicon have been studied. Implantation with dopant ions does not significantly affect the light emitting properties of LEPSi up to a dose of 10^{13} – 10^{14} cm $^{-2}$ although it changes the resistivity. At higher doses and for implantation with silicon or other ions that do not provide doping, the PL is quenched. These results are valuable for the fabrication of better LEPSi devices.

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